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Preparation and Electrochemical Properties of C/$LiMnPO_4$ for Lithium-Ion Battery by Spray Pyrolysis

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Abstract. Spherical C/$LiMn_{1-X}M_XPO_4$ (M=Mg, Zn) cathode materials were successfully prepared by spray pyrolysis. An olivine structure was obtained by heating at 973 K under argon/hydrogen (5%) atmosphere. Citric acid was used as the carbon source. Scanning electron microscopy (SEM) showed that the materials had spherical morphology. The electrochemical properties of the cathode were also estimated by the rechargeable capacity and cycle performance. The first discharge capacity of C/$LiMn_{1-X}Zn_XPO_4$ (X = 0.1) was approximately 60 mAh/g at 0.1 C.

Introduction

Recently, lithium oxides have attracted considerable attention as cathode materials for lithium-ion batteries in both electric vehicles (EVs) and hybrid vehicles (HEVs). $LiMn_2O_4$, $LiCoO_2$, and $LiMnPO_4$ have been studied as cathode materials for lithium-ion batteries. $LiCoO_2$ has high capacity and action voltage but is also expensive. Olivine-type lithium oxides are potential cathode materials for lithium-ion batteries because of their low cost, relatively high theoretical capacity of 170 mAh/g, and stable cycle performance at high temperature. Olivine-type $LiMnPO_4$ has been investigated as a cathode material for lithium-ion batteries because of their low cost, environmental friendliness, and high thermal stability, and good electrochemical performance. However, the electrochemical conductivity of $LiMnPO_4$ is too exiguous for it to be used as a cathode material. Therefore, most researchers have focused on improving the electrochemical conductivity of $LiMnPO_4$ by metal doping or coating with electrically conductive materials such as carbon [1,2]. Spray pyrolysis is considered to be suitable for the as-prepared process. The advantages of spray pyrolysis are (1) particle size control from micrometers to nanometers, (2) homogeneous composition, (3) low cost and energy consumption, and (4) high-speed production [3-5]. In this study, spherical C/$LiMnM_XPO_4$ (M = Mg, Zn) composite powders were prepared by spray pyrolysis using citric acid as a carbon source. Their physical chemistry characteristics and the electrochemical properties of $LiMnPO_4$ were investigated.

Experimental

$LiNO_3$, $Mn(NO_3)_2{\cdot}6H_2O$, and H_3PO_4 were used as materials for $LiMnPO_4$. $Zn(NO_3){\cdot}9H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ were used as a doping source for C/$LiMn_{1-X}M_XPO_4$ (M = Mg, Zn). These reagents

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were dissolved in distilled water. The molar ratio of the metal component (Li:Mn:M:P) was set to 1:1 - X:X:1 (X = 0.01, 0.05, 0.10) in the starting solution. Citric acid was added as a carbon source to aqueous solutions up to 100 mass%. The solution concentration was 0.1 mol/dm^3. The solution containing aqueous metal salts was misted at a frequency of 1.6 MHz by an ultrasonic nebulizer at a flow rate of 8 dm^3/min of air carrier gas. The electric furnace temperature was in the range of 523 to 773 K. C/$LiMn_{1-X}M_XPO_4$ (M = Mg, Zn) as-prepared precursor powders were continuously collected using a cyclone. The precursor powders were then calcined at 973 K for 3 h in an electric furnace under argon/hydrogen (5%) atmosphere. The crystal phases of the precursor powders and calcined powders were observed by powder X-ray diffraction (XRD, Shimadzu, XRD-6100) using CuKα radiation. The thermal behavior of $LiMnPO_4$, $LiMn_{1-X}M_XPO_4$ (M = Mg, Zn) and C/$LiMn_{1-X}M_XPO_4$ (M = Mg, Zn) were observed using a thermo gravimetric-differential analysis equipment (TG-DTA, SHIMADZU, DTG-60/60H) under an air atmosphere. The morphology and average particle size were determined with a scanning electron microscope (SEM, JEOL, JSM-6390). The cathode materials were prepared using 80 mass% calcined powders, 10 mass% acetylene black as a transmission, and 10 mass% polyvinylidenefluoride as a binder with 1-methyl-2-pyrrolidi-none (NMP). The slurry was coated on an aluminum foil and then dried at 373 K for 24 h. Celgard (Heist, Celgard 2400) was used as a separator. A solution of 1 mol/dm^3 $LiPF_6$ in ethylene carbonate/1, 2-dimethoxyethane (EC/DEC = 1:1, Tomiyama Pure Chemical) was used as the electrolyte. Metal lithium (Honjo Chemical) was used as an anode. The electrochemical properties of the products were examined using a CR2032-type coin cell. These coin cells were set up in globe box under argon atmosphere. The rechargeable capacity and cycle stability of the C/$LiMn_{1-X}M_XPO_4$ cathode were measured with a battery tester (Hosen, BTS2004) between 2.0 and 4.6 V.

Results and discussion

The crystal phase and crystallinity of C/$LiMn_{1-X}M_XPO_4$ (M = Mg, Zn) powders were identified by XRD. Figure 1 shows XRD patterns of C/$LiMn_{1-X}M_XPO_4$ (M = Mg, Zn, X = 0, 0.1) powders obtained by calcining at 973 K for 3 h. The crystal phases of all samples had an olivine structure with a Pmnb space group; no impurity phase peak was observed. The crystallinity of pure $LiMnPO_4$ was higher than that of C/$LiMn_{1-X}M_XPO_4$ (M = Mg, Zn). Therefore, no evidence for diffraction peaks for crystalline carbon appeared in the diffraction patterns throughout the temperature range; this indicates that the carbon generated from organic materials was amorphous carbon and that the presence of carbon did not influence the crystal structure of $LiMnPO_4$. The thermal behavior of $LiMnPO_4$, $LiMn_{1-X}M_XPO_4$ (M = Mg, Zn) and C/$LiMn_{1-X}M_XPO_4$ (M = Mg, Zn) were observed using a TG-DTA under an air atmosphere. The weight loss of $LiMnPO_4$ and $LiMn_{1-X}M_XPO_4$ (M = Mg, Zn) were not observed. On the other hands, when the exothermic reaction of C/$LiMn_{1-X}M_XPO_4$ (M = Mg, Zn) was observed between 573 K and 773 K, the weight loss of C/$LiMn_{1-X}M_XPO_4$ (M = Mg, Zn) was 10 mass%. It was found that decomposition of carbon obtained from citric acid led to the weight loss of C/$LiMn_{1-X}M_XPO_4$ (M = Mg, Zn). Figure 2 shows the SEM photographs of

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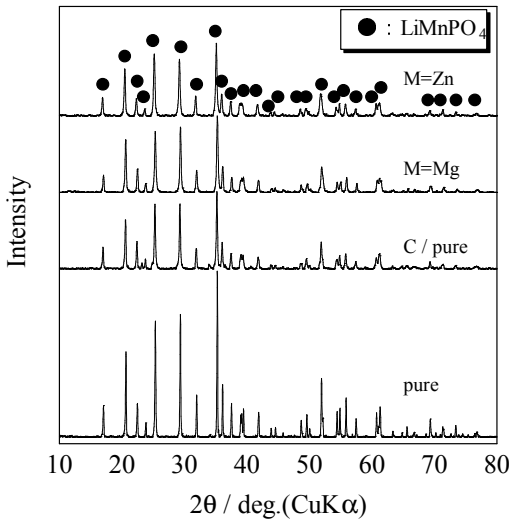

Fig. 1 XRD patterns of $C/LiMn_{1-X}M_XPO_4$ (M = Mg, Zn) powders

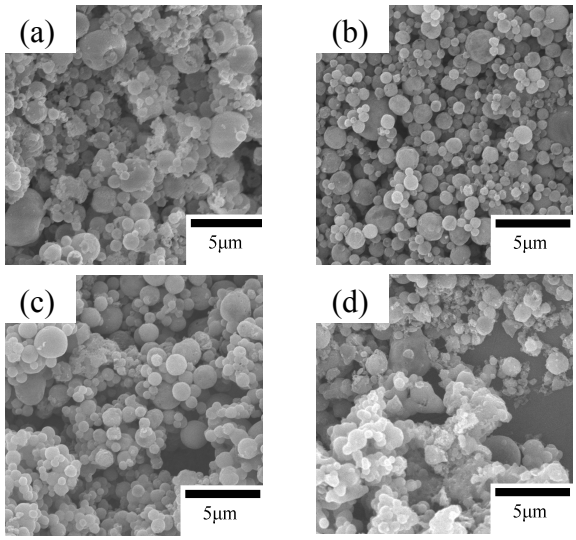

Fig. 2 SEM photographs of $C/LiMn_{1-X}M_XPO_4$ powders. (a) $LiMnPO_4$, (b) $C/LiMnPO_4$, (c) M = Mg, (d) M=Zn

$C/LiMn_{1-X}M_XPO_4$ (M = Mg, Zn, X = 0, 0.1) powders obtained by calcining at 973 K for 3 h under argon/hydrogen (5%) atmosphere. The pure $LiMnPO_4$ and $C/LiMn_{1-X}Zn_XPO_4$ powders had irregular particle morphology. In contrast, $C/LiMnPO_4$ and $C/LiMn_{1-X}Mg_XPO_4$ powders had spherical particle morphology. The addition of carbon did not change the spherical particle morphology. The average particle size of pure $LiMnPO_4$ was approximately 0.8 μm, and that of $C/LiMnPO_4$ was approximately 0.7 μm. The particle size of $C/LiMnPO_4$ was smaller than that of pure $LiMnPO_4$; as a result, pure $LiMnPO_4$ cohered. The average particle size of $C/LiMn_{1-X}M_XPO_4$ (M = Mg, Zn) was 0.7 to 0.8 μm. The average particle sizes of all samples were approximate. Figure 3 shows the first charge and discharge capacities of pure $LiMnPO_4$ and $C/LiMn_{1-X}M_XPO_4$ (M = Mg, Zn, X = 0, 0.1) cathodes at a rate of 0.1 C. The discharge capacity of pure $LiMnPO_4$ was 2 $mAhg^{-1}$, and that of $C/LiMnPO_4$ was 16 $mAhg^{-1}$. The electrical conductivity of pure $LiMnPO_4$ was 10^{-9} S/cm, whereas that of $C/LiMnPO_4$ was 10^{-5} S/cm. The discharge capacity may have increased by carbon doping, which in turn improved the electrochemical conductivity. The discharge capacity of $C/LiMn_{1-X}Mg_XPO_4$ barely changed with a change in the Mg-doped volume. The discharge capacity of $C/LiMn_{0.9}Mg_{0.1}PO_4$ was 40 $mAhg^{-1}$. The discharge capacity of $C/LiMn_{1-X}Zn_XPO_4$ increased with the increase in the Zn-doped volume. The discharge capacity of $C/LiMn_{0.9}Zn_{0.1}PO_4$ was 60 $mAhg^{-1}$. Figure 4 shows the cycle performance of $C/LiMn_{1-X}Mg_XPO_4$ at 298 K. The discharge capacity rate was maintained at a sufficiently good value as the Mg-doped volume increased.

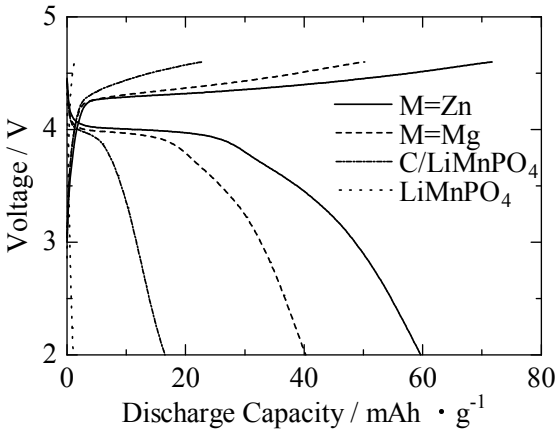

Fig. 3 First charge and discharge capacity of $LiMnPO_4$ and $C/LiMn_{1-X}M_XPO_4$(M=Mg, Zn, X=0, 0.1)

After 100 cycles, 97% of the initial discharge capacity was maintained at the rate of 0.1 C. Figure 5 shows the cycle performance of C/$LiMn_{1-X}Zn_XPO_4$ at 298 K. The discharge capacity rate was maintained at a sufficiently good value with an increase in the Zn-doped volume. After 100 cycles, 97% of the initial discharge capacity was maintained at the rate of 0.1 C. The discharge capacity of C/$LiMn_{1-X}M_XPO_4$ (M = Mg, Zn) powders derived from citric acid was found to result in stable

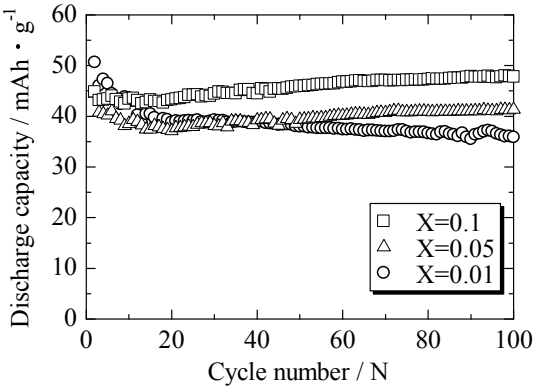

Fig. 4 Cycle performance of C/$LiMn_{1-X}Mg_XPO_4$ (X = 0.01, 0.05, 0.1)

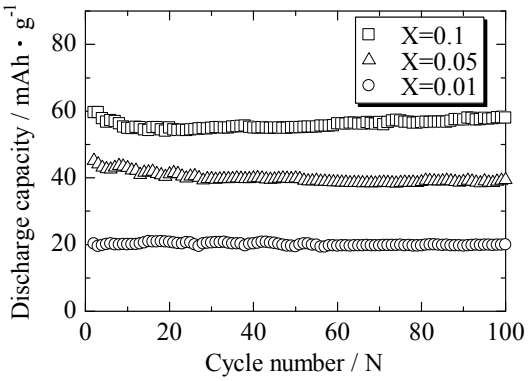

Fig. 5 Cycle performance of C/$LiMn_{1-X}Zn_XPO_4$ (X = 0.01, 0.05, 0.1)

cycle performance, and the results demonstrated improved electrical conductivity with carbon and metal material doping. However, these materials were essential for improving the electrical conductivity of the cathode material.

Conclusion

C/$LiMn_{1-X}M_XPO_4$ (M=Mg, Zn) precursor particles were successfully prepared by spray pyrolysis using aqueous solution with citric acid. The crystal phase of C/$LiMn_{1-X}M_XPO_4$ (M = Mg, Zn) had an olivine structure. Spherical particles were obtained. The electrochemical properties of $LiMnPO_4$ were improved by the addition of carbon. The discharge capacity of C/$LiMn_{1-X}Zn_XPO_4$ increased with the Zn-doped volume. From electrochemical measurements, the discharge capacity of $LiMn_{0.9}Zn_{0.1}PO_4$ was found to be 60 mAh/g at 0.1 C and resulted in a stable cycle performance at 298 K.

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